FORM PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

Rec'd PCT/PTO 30 OCT 2001
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ATTORNEY DOCKET NUMBER	U.S. APPLICATION NO (IF KNOWN SEE 37 RR 15)	
IN-12097		
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP 00/ 03466	17.04.00	30.04.99

PRODUCTION OF POLYURETHANE FOAMS

Andreas ALT; Dieter RODEWALD; Peter HORN; and Stephan BAUER.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.

2. [ ] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.

3. [ ] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1).

4. [ ] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date

5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   - a. [X] are transmitted herewith (required only if not transmittal by the International Bureau).
   - b. [ ] have been transmitted by the International Bureau.
   - c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US)

6. [X] A translation of the International Application into English (35 U.S.C. 371(C)(2)).

7. [X] Amendment to the claims of the International Application under PCT Article 19 (35 U.S.C.371(c)(3))
   - a. [X] are transmitted herewith (required only if not transmitted by the International Bureau).
   - b. [ ] have been transmitted by the International Bureau.
   - c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   - d. [ ] have not been made and will not be made

8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. [ ] A translation of the annex to the International Preliminary Examination Report under PCT Article 36

Items 11. to 16. below concern other document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included

13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.

14. [ ] A substitute specification.

15. [ ] A Change of power of attorney and/or address letter.

16. [X] Other items or information: Postcard

A copy of the cover sheet from the PCT Published Application
Notification of the Recording of a Change (Form PCT/1B/306)

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee" Mailing Label

No.EL 900586188US addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231

on 10/30/2001

Linda J. Cochran

LINDA J. COCHRAN

U.S. APPLICATION NO. (If known see 37 C.F.R. 1..	INTERNATIONAL APPLICATION NO. PCT/EP 00/003466	ATTORNEY'S DOCKET NUMBER IN-12097

17. [X] The following fees are submitted		CALCULATIONS | PTO USE ONLY	
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO	**$890.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.482)	**$710.00**		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))	**$740.00**		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO	**$1,040.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	**$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT	=	$890.00	
Surcharge of $130.00 for furnishing the oath or declaration later than [ ] 20 [X] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		$	

Claims	Number Filed	Number Extra	Rate		
Total Claims	6 - 20 =	0	X $18.00	$0.00	
Independent claims	2 - 03 =	0	X $84.00	$0.00	
Multiple dependent claims(s) (if applicable)			+ $280.00	$0.00	
TOTAL OF ABOVE CALCULATION			=	$890.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	
SUBTOTAL			=	$890.00	
Processing fee of $130.00 for furnishing the English translation later the [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).			+	$	
TOTAL NATIONAL FEE			=	$890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00 per property**			+	$40.00	
TOTAL FEES ENCLOSED			=	$930.00	
				Amount to be: Refunded	$
				Charged	$930.00

a. [ ] A check in the amount of $_____ to cover the above fees is enclosed.

b. [X] **Please charge my Deposit Account No. 23-3425 in the amount of $930.00 to cover the above fees A triplicate copy of this sheet is enclosed.**

c. [X] **The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-3425. A triplicate copy of this sheet is enclosed.**

NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

BASF CORPORATION
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1609 Biddle Avenue
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SIGNATURE
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Name
34,780
REGISTRATION NUMBER

Form PTO-1390(REV 5-93)

PATENT

(Docket No. IN-12097)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

ANDREAS ALT
ET AL

Serial No.: NEW

Filed: HEREWITH

For: PRODUCTION OF POLYURETHANE FOAMS

Group Art Unit: NEW

Examiner: NEW

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee" addressed to Commissioner of Patents and Trademarks, Washington, D.C. 20231, on 10/30/01.

Express Mail No. EL900586188US

Linda J. Cochran

PRELIMINARY AMENDMENT

BOX PCT APPLICATION
Assistant Commissioner of Patents
Washington, D.C. 20231

Sir:

In reference to the above-referenced patent application, please enter the following amendment and consider the accompanying remarks prior to examination thereof on the merits.

IN THE CLAIMS:

Please amend the claims as follows:

1. (Amended) A process for producing polyurethane foams comprising reacting isocyanates with compounds which are reactive toward isocyanates in the presence of blowing agents and in the presence or absence of catalysts, additives and/or auxiliaries,

wherein the reaction is carried out in the presence of at least one of the following compounds (i): an α, ß-unsaturated carboxylic acid, an α, ß-unsaturated carboxylic acid derivative, an α, ß-unsaturated ketone and an α, ß-unsaturated aldehyde.

2. (Amended) A process as claimed in claim 1, wherein the compound (i) comprises a compound having the formula $R^1R^2 - C = CR^3COR^4$, where

R^1 : H, $C_1 - C_{12}$ – alkyl, or $C_6 - C_{20}$ – aryl,

R2 : H, $C_1 - C_{12}$ – alkyl, or $C_6 - C_{20}$ – aryl,

R^3 : H, $C_1 - C_{12}$ – alkyl, or $C_6 - C_{20}$ – aryl,

R^4 : H, $C_1 - C_{12}$ – alkyl, or $C_6 - C_{20}$ – aryl, -O – $C_1 - C_{12}$ – alkyl,

-O – $C_1 - C_{12}$ – alkyl – OH, – $C_1 - C_{12}$ – alkyl – OH, -O – $C_1 - C_{12}$ – alkyl,

-O – $C_1 - C_{12}$ – alkyl $–NH_2$,

-$C_1 - C_{12}$ – alkyl $–NH_2$, -O-Benzyl, -O-Aryl,

-O - C_1-C_{12} – alkyl – COOH,

-O- C_1-C_{12} – alkyl – CH(OH) – CH_2 – O – (CO) – $CHCH_2$,

-O – $C_1 - C_{12}$ – alkyl – O – (CO) – $CHCH_2$, or

-O – $C_1 - C_{12}$ – alkyl – CH(OH) – $C_1 - C_{12}$ – alkyl – O – $C_1 - C_{12}$ – alkyl –

O – $C_1 - C_{12}$ – alkyl – CH(OH) – CH_2 – O – (CO) – $CHCH_2$.

3. (Amended) A process as claimed in claim 1, wherein the compound (i) comprises at least one of acrylic acid, crotonic acid, isocrotonic acid, sorbic acid, fumaric acid, cinnamic acid, hydroxyethyl acrylate, 3-(acryloyl-oxy)-2-hydroxypropyl methacrylate, benzyl cinnamate, trans-3-nonen-2-one, benzalacetone, dibenzalacetone, benzalacetophenone, 1-methylbenzalacetophenone, crotonaldehyde, cinnamaldehyde,

methyl vinyl ketone and an α, ß-unsaturated polyester diol prepared by polycondensation of maleic acid, fumaric acid, methacrylic acid and/or acrylic acid with oligomeric diols having a molecular weight factor per double bond of from 150 to 3000, a functionality of from 2 to 6, a hydroxyl number of from 20 to 800 and an acid number of from 0 to 15.

4. (Amended) A process as claimed in claim 1, wherein compound (i) is used in an amount of from 0.01 to 20% by weight, based on the weight of the polyurethane foam.

5. (Amended) A flexible polyurethane foam obtained in accordance with a process as claimed in claim 1.

6. (Amended) A flexible polyurethane foam comprising products of the reaction of primary and/or secondary amines with α, ß-unsaturated carboxylic acids, α, ß-unsaturated carboxylic acid derivatives, α, ß-unsaturated ketones and/or α, ß-unsaturated aldehydes.

REMARKS

Applicants respectfully request examination of the present application as amended herein. Claims 1-6 have been amended. Upon entry of the above preliminary amendment, claims 1-6 remain pending in the application. A marked-up version of the amended claims is attached hereto in Appendix A. Should the Examiner have any questions, please contact the undersigned attorney.

Respectfully submitted,

Date: Oct 30, 2001

Fernando A. Borrego
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APPENDIX A

1. (Amended) A process for producing [upholstery for furniture or automobiles, mattresses, foam backing for carpets,] polyurethane foams [for backfoaming instrument panels or steering wheels or shoe soles based on flexible polyurethane foams by] comprising reacting isocyanates with compounds which are reactive toward isocyanates in the presence of blowing agents and in the presence or absence of catalysts, additives and/or auxiliaries, wherein the reaction is carried out in the presence of at least one of the following compounds (i): an α, ß-unsaturated carboxylic acid, an α, ß-unsaturated carboxylic acid derivative, an α, ß-unsaturated ketone and[/or] an α, ß-unsaturated aldehyde.

2. (Amended) A process as claimed in claim 1, wherein the compound (i) [used is] comprises a compound having the formula $R^1R^2 - C = CR^3COR^4$, where

R^1 : H, $C_1 - C_{12}$ – alkyl, or $C_6 - C_{20}$ – aryl,

R2 : H, $C_1 - C_{12}$ – alkyl, or $C_6 - C_{20}$ – aryl,

R^3 : H, $C_1 - C_{12}$ – alkyl, or $C_6 - C_{20}$ – aryl,

R^4 : H, $C_1 - C_{12}$ – alkyl, or $C_6 - C_{20}$ – aryl, -O – $C_1 - C_{12}$ – alkyl,

-O – $C_1 - C_{12}$ – alkyl – OH, – $C_1 - C_{12}$ – alkyl – OH, -O – $C_1 - C_{12}$ – alkyl,

-O – $C_1 - C_{12}$ – alkyl $–NH_2$,

$-C_1 - C_{12}$ – alkyl $–NH_2$, -O-Benzyl, -O-Aryl,

-O - C_1-C_{12} – alkyl – COOH,

-O- C_1-C_{12} – alkyl – CH(OH) – CH_2 – O – (CO) – $CHCH_2$,

$-O-C_1-C_{12}-alkyl-O-(CO)-CHCH_2$, or

$-O-C_1-C_{12}-alkyl-CH(OH)-C_1-C_{12}-alkyl-O-C_1-C_{12}-alkyl-$

$O-C_1-C_{12}-alkyl-CH(OH)-CH_2-O-(CO)-CHCH_2$.

3. (Amended) A process as claimed in claim 1, wherein the compound (i) comprises at least one of acrylic acid, crotonic acid, isocrotonic acid, sorbic acid, fumaric acid, cinnamic acid, hydroxyethyl acrylate, 3-(acryloyl-oxy)-2-hydroxypropyl methacrylate, benzyl cinnamate, trans-3-nonen-2-one, benzalacetone, dibenzalacetone, benzalacetophenone, 1-methylbenzalacetophenone, crotonaldehyde, cinnamaldehyde, methyl vinyl ketone and[/or] an α, ß-unsaturated polyester diol prepared by polycondensation of maleic acid, fumaric acid, methacrylic acid and/or acrylic acid with oligomeric diols [such as butanediol, diethylene glycol, propylene glycol or 1,3-propanediol and/or triols such as glycerol and] having a molecular weight factor per double bond of from 150 to 3000, a functionality of from 2 to 6, a hydroxyl number of from 20 to 800 and an acid number of from 0 to 15.

4. (Amended) A process as claimed in claim 1, wherein compound (i) is used in an amount of from 0.01 to 20% by weight, based on the weight of the polyurethane foam.

5. (Amended) [Upholstery for furniture or automobiles, mattresses, foam backing for carpets, polyurethane foams for backfoaming instrument panels or steering wheels or shoes soles based on] A flexible polyurethane foam[s obtainable by] obtained in accordance with a process as claimed in claim 1.

6. (Amended) [Upholstery for furniture or automobiles, mattresses, foam backing for carpets, polyurethane foams for backfoaming instrument panels or steering wheels or

shoes soles based on] A flexible polyurethane foam[s] comprising products of the reaction of primary and/or secondary amines with α, ß-unsaturated carboxylic acids, α, ß-unsaturated carboxylic acid derivatives, α, ß-unsaturated ketones and/or α, ß-unsaturated aldehydes.

Production of polyurethane foams

The present invention relates to a process for producing polyurethane foams by reacting isocyanates with compounds which are reactive toward isocyanates in the presence of blowing agents and in the presence or absence of catalysts, additives and/or auxiliaries and also to the use of α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid derivatives, α,β-unsaturated ketones and/or α,β-unsaturated aldehydes in polyurethane foams.

The production of polyisocyanate polyaddition products, for example polyurethanes which may contain urea and/or isocyanurate structures, by reacting polyisocyanates with compounds which are reactive toward isocyanates in the presence of catalysts which accelerate the reaction of the isocyanate-reactive substances with isocyanates and in the presence or absence of blowing agents, additives and/or auxiliaries is generally known.

Like other synthetic polymers, polyisocyanate polyaddition products are subjected to ageing processes which generally lead to impairment of the use properties as time goes on. Significant ageing influences are, for example, hydrolysis, photooxidation and thermooxidation which lead to rupture of bonds in the polymer chains. In the case of polyisocyanate polyaddition products, for example polyurethanes, hereinafter also referred to as PURs, the action of moisture and even more the combination of moisture and elevated temperature results in hydrolytic cleavage of the urethane and urea bonds.

This cleavage not only leads to a significant deterioration in the use properties but also leads to formation of aromatic amines such as toluenediamine (TDA) and diaminodiphenylmethane (MDA) or aliphatic amines such as hexamethylenediamine or isophoronediamine.

As experiments have shown, the amine formation is influenced by a series of parameters. In particular, high temperatures above 80°C in combination with high atmospheric humidity lead to hydrolytic cleavage of the urethane and urea bonds. Such conditions are important in some specific application areas for flexible PUR foams.

A further parameter which has a significant influence on the formation of primary amines is the type and amount of catalysts used. As has been confirmed in various experiments, the catalysts

which are present in polyurethane systems and are necessary for the urethane formation and blowing reactions also catalyze the hydrolytic backdissociation reaction to a considerable extent. The presence of catalysts is thus a quite decisive prerequisite for the hydrolysis of the urethane and urea bonds. Furthermore, it has been able to be shown that the efficiency of the hydrolysis is highly dependent on the activity and type of catalyst and also on whether the catalyst remains in the system or can migrate out of the material. Especially tertiary amine catalysts containing reactive functional groups such as OH and NH_2 considerably accelerate amine formation by lowering the activation energy for the cleavage reaction. The functional groups result in incorporation of the catalysts into the PUR network formed and the products produced in this way have the advantage of lower odor and fogging problems since the catalysts cannot escape by diffusion after manufacture of the PUR products. The same applies to formulations comprising polyols which have been prepared using primary or secondary amines as initiator molecules and are thus catalytically active in the foam. Such foams have been increasingly used in recent times. In the case of formulations which comprise such constituents and in specific applications are exposed to particularly hot and humid conditions, the formation of primary amines as dissociation products cannot be ruled out. In contrast, in the case of foams containing amine catalysts having no functional groups which can be built into the foam, the catalysts are generally given off from the foam within a short time of manufacture or during the ageing of the foam. In the case of such foams, hot and humid conditions lead to significantly lower amine contents.

In order to reduce the occurrence of primary amines specifically in the case of PUR products which are exposed to hot and humid conditions, it was necessary to find additives which react with primary amine dissociation products to form chemically more acceptable compounds. These additives should not significantly influence the foaming reaction.

As compounds which reduce the content of primary aromatic amines in flexible polyurethane foams, stearically hindered cycloaliphatic monoisocyanates and monothioisocyanates are used according to US 4211847, GB 1565124 and DE-A 2946625. Owing to their stearic hindrance and their lower reactivity compared to aromatic isocyanates, these isocyanates react to only a small extent during the foaming reaction, so that free isocyanate is available after the foaming reaction is complete to react with any aromatic amines present. Disadvantages of these known teachings are that the compounds specified are relatively

expensive and that especially the two last-named compounds participate to at least some extent in the urethane formation reaction despite their steric hindrance and do not only react with aromatic amine formed after the foaming reaction. In addition, these isocyanates tend, owing to their low vapor pressure, to migrate out of the finished foam and thus represent a further health hazard due to the release of free isocyanate.

US 5821292 describes 3-arylacrylic esters as light stabilizers, oxidation inhibitors and heat stabilizers for organic polymers. This document does not discuss an improvement in the hydrolytic stability and especially a reaction with primary aromatic and aliphatic amines.

DE-A 42 32 420 discloses the use of α,β-unsaturated ester carboxylates for producing polyurethane foams which have an improved compressive strength and elongation at break. In this document, salts of α,β-unsaturated ester carboxylates are used as catalysts for the NCO/water reaction. In a subordinate clause, it is stated that the compounds are, owing to the presence of olefinic double bonds in the vicinity of the carboxylate groups, capable of addition onto amino groups which are formed during the slow ageing of the foam. A disadvantage of these compounds is their catalytic action which has an adverse effect on the foaming reaction. A catalytic action of additives to reduce the amine contents in finished PUR foams is undesirable since, as described above, it leads to further and accelerated formation of primary amines.

It is an object of the present invention to develop a process for producing polyurethane foams, which may include isocyanurate and/or urea structures, preferably flexible polyurethane foams, by reacting isocyanates with compounds which are reactive toward isocyanates in the presence of blowing agents and in the presence or absence of catalysts, additives and/or auxiliaries, which process makes it possible to decrease the content of, in particular, primary amines formed by hydrolytic cleavage of urethane and urea bonds by chemical reaction. In particular, additives which are able to reduce the content of primary, preferably primary aromatic, amines in flexible PUR foams are to be found. The amine traps should as far as possible be inexpensive and readily available and should act in the finished foam without further after-treatment. The compounds (i) should preferably have a vapor pressure which is not too low in order to avoid migration from the foam.

We have found that this object is achieved by carrying out the reaction in the presence of at least one of the following compounds (i): an α,β-unsaturated carboxylic acid, an α,β-unsaturated carboxylic acid derivative, an α,β-unsaturated ketone and/or an α,β-unsaturated aldehyde.

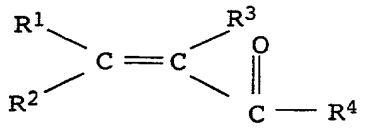
As a result of the use according to the present invention of compound (i), any free amino groups formed by undesired cleavage of urethane and/or urea bonds are bound by reaction with the novel compounds (i).

Both primary and secondary amines are capable of adding onto C=C double bonds, particularly when the latter are in the vicinity of a carbonyl group. The Michael addition of the amine occurs onto the unsaturated system in which the π electrons are delocalized over the carbonyl group. As has been established in experiments, temperatures of from 70 to 120°C, as can occur under hot and humid conditions, for example in steam sterilization or cleaning with hot steam, are surprisingly sufficient to react primary amine formed in the PUR foam by hydrolytic cleavage of urethane and urea bonds at least partly with the compounds (i) used according to the present invention.

The compounds (i) are thus employed in polyurethane foams to react with amino groups. The amino groups are bound by addition onto the C=C double bonds and to the α,β-unsaturated carbonyl compounds used according to the present invention to form a covalent bond. The diffusion or migration of primary amines from the polyurethane foam can thus be reduced according to the present invention. This is particularly true if the compounds (i) are built into the polyurethane network formed due to the presence of groups which can be built in, e.g. OH or NH_2. In this way, not only are the compounds (i) fixed and their diffusion from the polyurethane foam thus prevented, but the primary amine bound to the compound (i) is also fixed.

As (i), it is possible to use generally known α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid derivatives, α,β-unsaturated ketones and/or α,β-unsaturated aldehydes.

Preference is given to compounds (i) which include the following structural feature:



where the radicals R^1 to R^4 have the following meanings:

R^1: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl,
R^2: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl,
R^3: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl,
R^4: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl, -O-C_1-C_{12}-alkyl, -O-C_1-C_{12}-alkyl-OH, -C_1-C_{12}-alkyl-OH, -O-C_1-C_{12}-alkyl, -C_1-C_{12}-alkyl-NH_2, -O-C_1-C_{12}-alkyl-NH_2, -O-benzyl, -O-aryl, -O-C_1-C_{12}-alkyl-COOH, -O-C_1-C_{12}-alkyl-CH(OH)-CH_2-O-(CO)-$CHCH_2$, -O-C_1-C_{12}-alkyl-O-(CO)-$CHCH_2$, -O-C_1-C_{12}-alkyl-CH(OH)-C_1-C_{12}-alkyl-O-C_1-C_{12}-alkyl-O-C_1-C_{12}-alkyl-CH(OH)-CH_2-O-(CO)-$CHCH_2$.

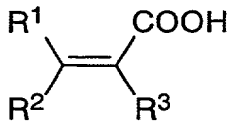
Particular preference is given to the following compounds as (i): acrylic acid, crotonic acid, isocrotonic acid, sorbic acid, fumaric acid, cinnamic acid, hydroxyethyl acrylate, 3-acryloyloxy-2-hydroxypropyl methacrylate, benzyl cinnamate, trans-3-nonen-2-one, benzalacetone, dibenzalacetone, benzalacetophenone, 1-methylbenzalacetophenone, crotonaldehyde, cinnamaldehyde, methyl vinyl ketone and/or α,β-unsaturated polyester diols prepared by polycondensation of maleic acid, fumaric acid, methacrylic acid and/or acrylic acid with oligomeric diols such as butanediol, diethylene glycol, propylene glycol or 1,3-propanediol and/or triols such as glycerol and having a molecular weight factor per double bond of from 150 to 3000, a functionality of from 2 to 6, a hydroxyl number of from 20 to 800 and an acid number of from 0 to 15.

Very particular preference is given to using the following compounds as (i): hydroxyethyl acrylate, 3-acryloyloxy-2-hydroxypropyl methacrylate, trans-3-nonen-2-one, benzyl cinnamate, crotonic acid and/or α,β-unsaturated polyester diols (A) prepared by polycondensation of maleic acid, fumaric acid, methacrylic acid or acrylic acid with oligomeric diols such as butanediol, diethylene glycol, propylene glycol or 1,3-propanediol and/or triols such as glycerol and having a molecular weight factor per double bond of from 150 to 3000, a functionality of from 2 to 6, a hydroxyl number of from 20 to 800 and an acid number of from 0 to 15.

Besides a pure polycondensation of an α,β-unsaturated carboxylic acid, preferably dicarboxylic acid, with diols and/or triols, the α,β-unsaturated polyester diols (A) can be prepared, for example,

by reaction of a polyhydric alcohol (B) with a compound (C) containing an epoxy function and additionally a functional group which is reactive toward alcohols to give a compound (D) and reaction of this compound (D) with an α,ß-olefinically unsaturated carboxylic acid (E) to form the compound (A) used according to the present invention or by direct reaction of an α,ß-olefinically unsaturated carboxylic acid (E) with (B) to give a compound (A). Suitable compounds (B) are polyhydric, in particular dihydric, alcohols. Use can advantageously be made of alcohols having from 2 to 30, preferably from 2 to 20, carbon atoms, e.g. diols such as 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-hexanediol, 1,8-octanediol, 1,10-decanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-methyl-2-butyl-1,3-propanediol, 2,2-dimethyl-1,4-butanediol, 2,3-dimethyl-2,3-butanediol, 2-butene-1,4-diol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,3-cyclohexanediol, menthol, 1,4-cyclohexanedimethanol, neopentyl glycol hydroxypivalate, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol or methyldiethanolamine and triols such as glycerol, trimethylolpropane or 1,2,4-butanetriol and alcohols having at least four hydroxy groups, e.g. pentaerythritol, sorbitol, threitol, mannitol or dulcitol or aromatic-aliphatic or aromatic-cycloaliphatic diols having from 8 to 30 carbon atoms, where possible aromatic structures are heterocyclic ring systems or preferably isocyclic ring systems such as naphthalene or in particular benzene derivatives, e.g. hydroquinone, 4,4'-dihydroxybiphenyl, bisphenol A, symmetrically diethoxylated bisphenol A, symmetrically dipropoxylated bisphenol A, higher ethoxylated or propoxylated bisphenol A derivatives or bisphenol F derivatives, commercial polyetherols such as Lupranol®, Pluracol® (BASF), Systol® (BASF), Baycoll® (Bayer), Caradol® (Shell), Arcol® (Lyondell), Varanol® (DOW Chemical), Polypol® (Polioles), Teracol® (Enichem), and also mixtures of such compounds. As compounds (C) which react with the hydroxyl groups of (B), it is possible to use many classes of substances, e.g. epoxidated olefins, glycidyl esters of saturated or unsaturated carboxylic acids, glycidyl ethers of aliphatic or aromatic polyols or epoxyalkyl halides. Examples of suitable compounds are (+)-1-chloro-2,3-epoxy-2-methyl-propane, (-)-1-chloro-2,3-epoxy-2-methylpropane, (1)-chloro-2,3-epoxy-2-methyl-propane, in particular (+)-1-chloro-2,3-epoxypropane, (-)-1-chloro-2,3-epoxypropane or (1)-chloro-2,3-epoxypropane, and also mixtures of such compounds. The reaction to form the compound (D) used according to the present invention can be carried out in a manner known per se, as described, for example, in C.A. May, Epoxy Resins Chemistry and

Technology, Marcel Dekker Inc., New York/Basle, 1988. Such compounds are known per se. Particular preference is given to polyglycidyl compounds of the bisphenol A type and glycidyl ethers of polyfunctional alcohols, e.g. of butanediol, of hexanediol, of neopentyl glycol, of 1,4-cyclohexanedimethanol, of glycerol and of pentaerythritol, for example Epikote 812, Epikote 828 and Epikote 162 from Shell or Heloxy 68 and Heloxy 107 from Rhône-Poulenc. The compound (D) can be isolated from the reaction mixture by known methods, e.g. by extraction, precipitation or spray drying, and advantageously used for preparing the compound (A). Suitable compounds (E) are first and foremost carboxylic acids of the formula (II)



(II)

where R^1, R^2 and R^3 are hydrogen or C_1-C_4-alkyl radicals; preference is given to maleic acid, fumaric acid, acrylic acid and methacrylic acid. It is also possible to use mixtures of various carboxylic acids of this type.

The reaction to form the compound (A) used according to the present invention can be carried out in a manner known per se, preferably at from 90 to 130°C, particularly preferably from 100 to 110°C, and advantageously until the reaction mixture has an acid number of less than 5 mg KOH/g.

Particular preference is given to the reaction of (B) with (E) to give the compound (A) used according to the present invention.

As catalysts for the reaction of a compound (D) with a compound (E), it is possible to use, for example, KOH, quaternary ammonium or phosphonium compounds, tertiary amines, phosphines such as triphenylphosphine or Lewis bases such as thiodiglycol.

The catalysts are preferably used in amounts of from 0.01 to 5% by weight, particularly preferably from 0.1 to 3% by weight, based on the compound (D).

The use of a solvent or diluent is not necessary, but is preferred.

Suitable solvents or diluents are hydrocarbons, in particular toluene, xylene or cyclohexane, esters, in particular ethyl glycol acetate, ethyl acetate or butyl acetate, amides, in particular dimethylformamide or N-methylpyrrolidone, sulfoxides,

in particular dimethyl sulfoxide, ketones, in particular methyl ethyl ketone or cyclohexanone, ethers, in particular diisopropyl ether or methyl tert-butyl ether, or preferably cyclic ethers, in particular tetrahydrofuran or dioxane. The solvents or diluents can be used individually or as a mixture.

To avoid premature polymerization, the reaction, particularly with acrylic acid or methacrylic acid, is advantageously carried out in the presence of small amounts of inhibitors. Possible inhibitors are the customary compounds used for preventing thermal polymerization, e.g. hydroquinone, hydroquinone monoalkyl ethers, 2,6-di-tert-butylphenol, N-nitrosamines of phenothiazines or phosphorous esters. They are generally used in amounts of from 0.005 to 0.5% by weight, based on the compound (E).

The compound (A) can be isolated from the reaction mixture by known methods, e.g. by extraction, precipitation, drying or spray drying.

As mentioned above, α,β-unsaturated carbonyl compounds having additional functional groups such as OH and NH_2 which are built into the PUR network lead to a particularly significant reduction in the MDA and TDA contents. Examples which may be mentioned are hydroxyethyl acrylate and 3-acryloyloxy-2-hydroxypropyl methacrylate. Polyols having integrated C=C double bonds conjugated with the carbonyl group have a similar action.

Particular preference is generally given to compounds (i) which dissolve readily in the isocyanates or the compounds which are reactive toward isocyanates. Preference is given to using (i) in admixture with the isocyanates.

In the process of the present invention for producing polyurethane foams, (i) is preferably used in an amount of from 0.1 to 20% by weight, particularly preferably from 0.5 to 10% by weight, based on the weight of the polyurethane foam.

The polyurethane foams obtainable according to the present invention have the particular advantage that any primary amines formed by hydrolysis, in particular primary aromatic amines, are converted by the compounds (i) into an unproblematical form. The polyurethane foams, in particular mattresses, furniture upholstery or foam backing of carpets, thus particularly preferably comprise products of the reaction of primary and/or secondary amines, preferably aromatic amines, with the abovementioned compounds (i), i.e. the α,β-unsaturated carboxylic

acids, α,β-unsaturated carboxylic acid derivatives, α,β-unsaturated ketones and/or α,β-unsaturated aldehydes.

Preference is accordingly given to the use of α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid derivatives, α,β-unsaturated ketones and/or α,β-unsaturated aldehydes in polyurethane foams having a reduced primary amine content, in particular by reaction of the compounds (i) with the amino groups in the polyurethane foams, i.e. the use of α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid derivatives, α,β-unsaturated ketones and/or α,β-unsaturated aldehydes in polyurethane foams to react with primary amines.

As isocyanates to be used in the process for producing polyurethane foams, it is possible to use, for example, the compounds described below:

Isocyanates which can be used are the aliphatic, cycloaliphatic, araliphatic and preferably aromatic organic isocyanates known per se, preferably polyfunctional isocyanates, particularly preferably diisocyanates.

Specific examples are: alkylene diisocyanates having from 4 to 12 carbon atoms in the alkylene radical, e.g. dodecane 1,12-diisocyanate, 2-ethyltetramethylene 1,4-diisocyanate, 2-methylpentamethylene 1,5-diisocyanate, tetramethylene 1,4-diisocyanate and preferably hexamethylene 1,6-diisocyanate; cycloaliphatic diisocyanates such as cyclohexane 1,3- and 1,4-diisocyanate and also any mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate), hexahydrotolylene 2,4- and 2,6-diisocyanate and also the corresponding isomer mixtures, dicyclohexylmethane 4,4'-, 2,2'- and 2,4'-diisocyanate and also the corresponding isomer mixtures, aromatic diisocyanates and polyisocyanates such as tolylene 2,4- and 2,6-diisocyanate (TDI) and the corresponding isomer mixtures, diphenylmethane 4,4'-, 2,4'- and 2,2'-diisocyanate (MDI) and the corresponding isomer mixtures, naphthalene 1,5-diisocyanate (NDI), mixtures of diphenylmethane 4,4'- and 2,4'-diisocyanates, mixtures of NDI and diphenylmethane 4,4'- and/or 2,4'-diisocyanates, 3,3'-dimethyl-4,4'-diisocyanatobiphenyl (TODI), mixtures of TODI and diphenylmethane 4,4'- and/or 2,4'-diisocyanates, polyphenylpolymethylene polyisocyanates, mixtures of diphenylmethane 4,4'-, 2,4'- and 2,2'-diisocyanates and polyphenylpolymethylene polyisocyanates (crude MDI) and mixtures of crude MDI and tolylene diisocyanates. The organic

diisocyanates and polyisocyanates can be used individually or in the form of their mixtures.

Use is frequently also made of modified polyfunctional isocyanates, i.e. products which are obtained by chemical reaction of organic diisocyanates and/or polyisocyanates. Examples which may be mentioned are diisocyanates and/or polyisocyanates containing ester, urea, biuret, allophanate, carbodiimide, isocyanurate, uretdione and/or urethane groups. Specific examples are: organic, preferably aromatic polyisocyanates containing urethane groups and having NCO contents of from 33.6 to 15% by weight, preferably from 31 to 21% by weight, based on the total weight, modified diphenylmethane 4,4'-diisocyanate, modified diphenylmethane 4,4'- and 2,4'-diisocyanate mixtures, modified NDI, modified TODI, modified crude MDI and/or tolylene 2,4- or 2,6-diisocyanate, with examples of dialkylene and polyoxyalkylene glycols which can be used individually or as mixtures being: diethylene glycol, dipropylene glycol, polyoxyethylene, polyoxypropylene and polyoxypropylene-polyoxyethylene glycols, triols and/or tetrols. Further suitable modified isocyanates are prepolymers containing NCO groups, having NCO contents of from 25 to 3.5% by weight, preferably from 21 to 14% by weight, based on the total weight, and prepared from, for example, polyester polyols and/or preferably polyether polyols and diphenylmethane 4,4'-diisocyanate, mixtures of diphenylmethane 2,4'- and 4,4'-diisocyanate, NDI, TODI, mixtures of NDI and isomers of MDI, tolylene 2,4- and/or 2,6-diisocyanates or crude MDI. Other modified isocyanates which have been found to be useful are liquid polyisocyanates containing carbodiimide groups and/or isocyanurate rings and having NCO contents of from 33.6 to 15% by weight, preferably from 31 to 21% by weight, based on the total weight, e.g. those based on diphenylmethane 4,4'-, 2,4'- and/or 2,2'-diisocyanate, NDI, TODI and/or tolylene 2,4- and/or 2,6-diisocyanate.

The modified polyisocyanates can, if desired, be mixed with one another or with unmodified organic polyisocyanates such as diphenylmethane 2,4'- and/or 4,4'-diisocyanate, NDI, TODI, crude MDI, tolylene 2,4- and/or 2,6-diisocyanate.

As isocyanates in the mixtures or process according to the present invention, preference is given to using diphenylmethane 4,4'-, 2,4'- and/or 2,2'-diisocyanate, tolylene 2,4- and/or 2,6-diisocyanate, NDI, hexamethylene diisocyanate and/or

isophorone diisocyanate; these isocyanates can be used both in any mixtures and in modified form as described above.

As compounds which are reactive toward isocyanates and usually have at least two reactive hydrogen atoms, customarily hydroxyl and/or amino groups, use is advantageously made of ones having a functionality of from 2 to 8, preferably from 2 to 6, and a molecular weight of usually from 60 to 10,000. Compounds which have been found to be useful are, for example, polyether polyamines and/or preferably polyols selected from the group consisting of polyether polyols, polyester polyols, polythioether polyols, polyesteramides, hydroxyl-containing polyacetals and hydroxyl-containing aliphatic polycarbonates or mixtures of at least two of the polyols mentioned. Preference is given to using polyester polyols and/or polyether polyols which can be prepared by known methods.

The polyester polyols preferably have a functionality of from 2 to 4, in particular from 2 to 3, and a molecular weight of usually from 500 to 3000, preferably from 1200 to 3000 and in particular from 1800 to 2500.

The polyether polyols have a functionality of preferably from 2 to 6 and usually have molecular weights of from 500 to 8000.

Suitable polyether polyols also include, for example, polymer-modified polyether polyols, preferably graft polyether polyols, particularly those based on styrene and/or acrylonitrile which can be prepared by in-situ polymerization of acrylonitrile, styrene or preferably mixtures of styrene and acrylonitrile.

Like the polyester polyols, the polyether polyols can be used individually or in the form of mixtures. They can also be mixed with the graft polyether polyols or polyester polyols and with hydroxyl-containing polyesteramides, polyacetals and/or polycarbonates.

Polyol components used for rigid polyurethane foams, which may, if desired, contain isocyanurate structures, are high-functionality polyols, in particular polyether polyols based on high-functionality alcohols, sugar alcohols and/or saccharides as initiator molecules while polyol components used for flexible foams are 2- and/or 3-functional polyether polyols and/or polyester polyols based on glycerol and/or trimethylolpropane and/or glycols as initiator molecules or alcohols to be esterified. The polyether polyols are prepared by known techniques. Examples of alkylene oxides which are suitable for

preparing the polyols are tetrahydrofuran, 1,3-propylene oxide, 1,2- or 2,3-butylene oxide, styrene oxide and preferably ethylene oxide and 1,2-propylene oxide. The alkylene oxides can be used individually, alternately in succession or as mixtures. Preference is given to using alkylene oxides which lead to primary hydroxyl groups in the polyol. Particularly preferred polyols are those which have been alkoxylated with ethylene oxide at the end of the alkoxylation and thus have primary hydroxyl groups. To produce thermoplastic polyurethanes, preference is given to using polyols having a functionality of from 2 to 2.2 and no crosslinkers.

Furthermore, chain extenders and/or crosslinkers can be used as compounds which are reactive toward isocyanates. The addition of chain extenders, crosslinkers or, if desired, mixtures thereof can prove to be advantageous for, for example, modifying the mechanical properties, e.g. the hardness, of the polyisocyanate polyaddition products produced using these substances. As chain extenders and/or crosslinkers, it is possible to use water, diols and/or triols having molecular weights of from 60 to < 500, preferably from 60 to 300. Suitable chain extenders/crosslinkers are, for example, aliphatic, cycloaliphatic and/or araliphatic diols having from 2 to 14, preferably from 4 to 10, carbon atoms, e.g. ethylene glycol, 1,3-propanediol, 1,10-decanediol, o-, m-, p-dihydroxycyclohexane, diethylene glycol, dipropylene glycol and preferably 1,4-butanediol, 1,6-hexanediol and bis(2-hydroxyethyl)hydroquinone, triols such as 1,2,4- and/or 1,3,5-trihydroxycyclohexane, glycerol and trimethylolpropane and low molecular weight hydroxyl-containing polyalkylene oxides based on ethylene oxide and/or 1,2-propylene oxide and diols and/or triols as initiator molecules.

If chain extenders, crosslinkers or mixtures thereof are employed for producing the polyisocyanate polyaddition products, they are advantageously used in an amount of from 0 to 20% by weight, preferably from 2 to 8% by weight, based on the weight of the compounds which are reactive toward isocyanates; thermoplastic polyurethanes are preferably produced without using crosslinkers.

For the purposes of the present invention, compounds which are reactive toward isocyanates are by definition considered only to include those which do not come under the definition of (i).

Suitable catalysts are generally customary compounds, for example organic amines such as triethylamine, triethylenediamine, tributylamine, dimethylbenzylamine, N,N,N',N'-tetramethylethylenediamine,

N,N,N',N'-tetramethylbutanediamine, N,N,N',N'-tetramethylhexane-1,6-diamine, dimethylcyclohexylamine, pentamethyldipropylenetriamine, pentamethyldiethylenetriamine, 3-methyl-6-dimethylamino-3-azapentol, dimethylaminopropylamine, 1,3-bis(dimethylamino)butane, bis(2-dimethylaminoethyl) ether, N-ethylmorpholine, N-methylmorpholine, N-cyclohexylmorpholine, 2-dimethylaminoethoxyethanol, dimethylethanolamine, tetramethylhexamethylenediamine, dimethylamino-N-methylethanolamine, N-methylimidazole, N-(3-aminopropyl)imidazole, N-(3-aminopropyl)-2-methylimidazole, 1-(2-hydroxyethyl)imidazole, N-formyl-N,N'-dimethylbutylenediamine, N-dimethylaminoethylmorpholine, 3,3'-bis(dimethylamino)di-n-propylamine and/or bis(2-piperazinoisopropyl) ether, dimethylpiperazine, N,N'-bis(3-aminopropyl)ethylenediamine and/or tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine, or mixtures comprising at least two of the abovementioned amines. It is also possible to use relatively high molecular weight tertiary amines as are described, for example, in DE-A 28 12 256. Further catalysts which can be used are organic metal compounds customary for this purpose, preferably organic tin compounds such as tin(II) salts of organic carboxylic acids, e.g. tin(II) acetate, tin(II) octoate, tin(II) ethylhexanoate and tin(II) laurate, and the dialkyltin(IV) salts of organic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate. Tertiary aliphatic and/or cycloaliphatic amines are preferably present in the mixtures; triethylenediamine is particularly preferably present.

As blowing agents, it is possible to use, preferably for producing foam polyurethanes, generally known blowing agents such as materials which have a boiling point at atmospheric pressure in the range from -40°C to 120°C, gases and/or solid blowing agents and/or water in customary amounts, for example carbon dioxide, alkanes and/or cycloalkanes such as isobutane, propane, n- or iso-butane, n-pentane and cyclopentane, ethers such as diethyl ether, methyl isobutyl ether and dimethyl ether, nitrogen, oxygen, helium, argon, nitrous oxide, halogenated hydrocarbons and/or partially halogenated hydrocarbons such as trifluoromethane, monochlorotrifluoroethane, difluoroethane, pentafluoroethane, tetrafluoroethane or mixtures comprising at least two of the blowing agents mentioned by way of example.

As auxiliaries and/or additives, mention may be made of, for example, surface-active substances, foam stabilizers, cell regulators, fillers, dyes, pigments, flame retardants, hydrolysis inhibitors, fungistatic and bacteriostatic substances.

The starting materials for producing the polyurethane foams have been described above by way of example. The organic polyisocyanates and the compounds which are reactive toward isocyanates and have a molecular weight of from 60 to 10,000 g/mol are usually reacted in such amounts that the equivalence ratio of NCO groups of the polyisocyanates to the sum of the reactive hydrogen atoms of the compounds which are reactive toward isocyanates is 0.5-5:1, preferably 0.9-3:1 and in particular 0.95-2:1.

It may be advantageous for the polyurethanes to contain at least some bound isocyanurate groups. In these cases, a ratio of NCO groups of the polyisocyanates to the sum of the reactive hydrogen atoms of 1.5-60:1, preferably 1.5-8:1, is preferably selected.

The polyurethane foams can be produced, for example, by the one-shot method or by the known prepolymer method, for example with the aid of high-pressure or low-pressure technology in open or closed molds, reaction extruders or belt units.

It has been found to be advantageous to produce the polyurethane foams by the two-component process and to combine the compounds which are reactive toward isocyanates and, if appropriate, the catalysts, blowing agents and/or auxiliaries and/or additives as the A component and to use the isocyanates and catalysts and/or blowing agents as B components.

The process of the present invention is preferably used for producing upholstery for furniture or automobiles, mattresses, in particular hospital mattresses, foam backing for carpets, PUR foams for backfoaming instrument panels or steering wheels or shoe soles.

The invention is illustrated by the following examples.

Examples

To simulate conditions which can occur in the specific applications mentioned above, ageing under hot and humid conditions was carried out on samples of the flexible foams described below. For this purpose, test cubes of the foams to be tested having an edge length of 3 cm were in each case aged at

90°C and 90% relative atmospheric humidity for 72 hours in an air-conditioned chamber. Under these conditions, it is possible for hydrolytic cleavage of urethane and urea bonds to occur, resulting in formation of primary aromatic amines. The amine formed was subsequently extracted by means of a method developed by Prof. Skarping, University of Lund. For this purpose, the foam was squeezed out 10 times with 10 ml of acetic acid (w = 1% by weight). With the foam specimen compressed, the acetic acid was transferred to a 50 ml volumetric flask. The procedure was repeated twice and the volumetric flask was made up to the mark with acetic acid. The MDA/TDA content of the combined extracts was subsequently determined by means of capillary electrophoresis with UV detection. The MDA/TDA contents reported in the table correspond to the absolute contents of MDA/TDA formed in the PUR foam.

Example 1

Production of a flexible polyurethane foam by mixing 750 g of A component with 354 g of B component (index: 90) and transferring the foaming mixture into an aluminum mold (40 x 40 x 10 cm) heated to 53°C, with the components having the following compositions:

A Component

97 parts of a polyol having a hydroxyl number (OHN) of 28 mg KOH/g, a mean functionality of 2.3 and an ethylene oxide (EO)/propylene oxide (PO) ratio of 14/86,

3 parts of a polyol having an OHN of 42 mg KOH/g, a mean functionality of 3 and a PO/EO ratio of 30/70,

3.31 parts of water,
0.8 part of aminopropylimidazole,
0.6 part of Lupragen® N 107, OHN: 421 (BASF Aktiengesellschaft),
0.5 part of Tegostab B 8631 (Goldschmidt).

B component

Mixture of 50% of a polymeric MDI and 50% of a bifunctional MDI mixture.

As catalysts which can be built into the polyurethane, this system contains aminopropylimidazole and Lupragen® N 107 (BASF Aktiengesellschaft). It was selected to show the particular effectiveness of the additives in PUR formulations containing

catalysts which can be built into the polyurethane and catalytically active spacer polyols, as illustrated by the significant reduction of the MDA contents of foams with addition of α,β-unsaturated carbonyl compounds compared to the comparative system in Table 1.

Table 1: Comparison of the MDA contents of flexible PUR foams without (foam 1) and with addition of α,β-unsaturated carbonyl compounds (foams 2 to 8)

Foam	1	2	3	4	5	6	7	8
Hydroxyethyl acrylate [% by weight to (A)]	-	10	-	-	-	-	-	-
3-(Acryloyloxy)-2-hydroxy-propyl methacrylate	-	-	10	-	-	-	-	-
Laromer® 8765 [% by weight to A]	-	-	-	10	-	-	-	-
Lupragen® VP 9198 [% by weight to A]	-	-	-	-	10	-	-	-
trans-3-Nonen-2-one [% by weight to (A)]	-	-	-	-	-	9.6	-	-
Benzyl cinnamate [% by weight to (B)]	-	-	-	-	-	-	7.2	-
Crotonic anhydride [% by weight to (B)]	-	-	-	-	-	-	-	2
Cream time [s]	13	15	15	15	20	15	25	20
Gel time [s]	80	90	95	95	95	85	95	95
Rise time [s]	100	110	150	115	110	120	120	140
4,4'-MDA [ppm] w.o.a.	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-MDA [ppm] w.o.a.	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-MDA [ppm] w.a.	397	31	59	55	43	223	155	98
2,4'-MDA [ppm] w.a.	687	86	134	118	105	391	321	184

(A): Addition of (i) to the polyol component
(B): Addition of (i) to the isocyanate component
w.o.a.: Extraction after processing of the foam
w.a.: Extraction after hot-humid ageing for 3 days at 90°C and 90% relative atmospheric humidity in an air-conditioned chamber

Laromer® 8765 (BASF Aktiengesellschaft): OH-containing bisacrylic ester having a molecular weight of 346.4 g/mol and an OHN of 323 mg KOH/g.

Lupragen® VP 9198 (BASF Aktiengesellschaft): α,β-unsaturated polyester diol having an OH number of 336 mg KOH/g, an acid number of 0.7 and a molecular weight factor per double bond of

262, prepared by polycondensation of maleic anhydride, 1,3-propanediol and diethylene glycol in a molar ratio of 1:1:1.

Example 2

Production of a flexible polyurethane foam which was employed as a model for standard flexible foams by mixing 750 g of A component with 349 g of B component (index: 90) and transferring the foaming mixture into an aluminum mold (40 x 40 x 10 cm) heated to 53°C; the components had the following compositions:

A component

97 parts of a polyol having an OHN of 28 mg KOH/g, a mean functionality of 2.3 and an EO/PO ratio of 14/86,

3 parts of a polyol having an OHN of 42 mg KOH/g, a mean functionality of 3 and a PO/EO ratio of 30/70,

3.31 parts of water,
0.22 part of 1,4-diazabicyclo[2.2.2]octane,
0.14 part of Lupragen® N 206 (BASF Aktiengesellschaft),
0.5 part of Tegostab B 8631 (Goldschmidt).

B component

Mixture of 50% of a polymeric MDI and 50% of a bifunctional MDI mixture.

Table 2: Comparison of the MDA contents of flexible PUR foams without (foam 9) and with addition of α,β-unsaturated carbonyl compounds (foams 10 and 11)

Foam	9	10	11
Hydroxyethyl acrylate [% by weight to (A)]	-	10	
Laromer® 8765 [% by weight to (A)]	-	-	10
Cream time[s]	13	15	-
Gel time [s]	45	70	-
Rise time [s]	80	-	-
4,4'-MDA [ppm] w.o.a.	<1	<1	<1
2,4'-MDA [ppm] w.o.a.	<1	<1	<1
4,4'-MDA [ppm] w.a.	32	20	25
2,4'-MDA [ppm] w.a.	78	57	64

(A): Addition of (i) to the polyol component
(B): Addition of (i) to the isocyanate component

w.o.a.: Extraction after processing of the foam
w.a.: Extraction after hot-humid ageing for 3 days at 90°C and 90% relative atmospheric humidity in an air-conditioned chamber

Example 3

Production of a flexible polyurethane foam by mixing 750 g of A component with 275 g of B component (index: 115) and transferring the foaming mixture to an open mold having a volume of 40 l; the components have the following compositions:

A component

100 parts of Lupranol® 2080 (BASF),
2.65 parts of water,
0.25 part of Lupragen® N 101 (BASF),
0.04 part of Lupragen® N 206 (BASF),
0.20 part of tin dioctoate,
0.80 part of silicone stabilizer BF 2370

B component

Lupranat® T 80 (BASF)

Table 3: Comparison of the TDA contents of flexible PUR foams without (foam 12) and with addition of α,β-unsaturated carbonyl compounds (foams 13 to 16)

Foam	12	13	14	15	16
Hydroxyethyl acrylate [% by weight to (A)]	-	5	-	-	-
3-(Acryloyloxy)-2-hydroxypropyl methacrylate [% by weight to (A)]	-	-	5	-	-
Laromer® 8765 (BASF AG) [% by weight to A]	-	-	-	10	-
Lupragen® VP 9198 (BASF AG) [% by weight to A]	-	-	-	-	10
2,4-TDA [ppm] w.o.a.	<1	<1	<1	<1	<1
2,6-TDA [ppm] w.o.a.	<1	<1	<1	<1	<1
2,4-TDA [ppm] w.a.	31	10	7	9	3
2,6-TDA [ppm] w.a.	8	6	4	5	2

(A): Addition of (i) to the polyol component
(B): Addition of (i) to the isocyanate component
w.o.a.: Extraction after processing of the foam

w.a.: Extraction after hot-humid ageing for 3 days at 90°C and 90% relative atmospheric humidity in an air-conditioned chamber

The detection limit of the capillary electrophoretic determination is 1 ppm.

The advantages obtained according to the present invention, i.e. the significantly lower content of primary aromatic amines after ageing under hot and humid conditions, could thus be convincingly demonstrated.

We claim:-

1. A process for producing polyurethane foams by reacting isocyanates with compounds which are reactive toward isocyanates in the presence of blowing agents and in the presence or absence of catalysts, additives and/or auxiliaries, wherein the reaction is carried out in the presence of at least one of the following compounds (i): an α,β-unsaturated carboxylic acid, an α,β-unsaturated carboxylic acid derivative, an α,β-unsaturated ketone and/or an α,β-unsaturated aldehyde.

2. A process as claimed in claim 1, wherein the compound (i) used is $R^1R^2-C=CR^3COR^4$, where

R^1: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl,
R^2: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl,
R^3: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl,
R^4: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl, -O-C_1-C_{12}-alkyl, -O-C_1-C_{12}-alkyl-OH, -C_1-C_{12}-alkyl-OH, -O-C_1-C_{12}-alkyl, -O-C_1-C_{12}-alkyl-NH_2, -C_1-C_{12}-alkyl-NH_2, -O-Benzyl, -O-Aryl, -O-C_1-C_{12}-alkyl-COOH, -O-C_1-C_{12}-alkyl-CH(OH)-CH_2-O-(CO)-$CHCH_2$, -O-C_1-C_{12}-alkyl-O-(CO)-$CHCH_2$, -O-C_1-C_{12}-alkyl-CH(OH)-C_1-C_{12}-alkyl-O-C_1-C_{12}-alkyl-O-C_1-C_{12}-alkyl-CH(OH)-CH_2-O-(CO)-$CHCH_2$.

3. A process as claimed in claim 1, wherein the compound (i) used is acrylic acid, crotonic acid, isocrotonic acid, sorbic acid, fumaric acid, cinnamic acid, hydroxyethyl acrylate, 3-(acryloyl-oxy)-2-hydroxypropyl methacrylate, benzyl cinnamate, trans-3-nonen-2-one, benzalacetone, dibenzalacetone, benzalacetophenone, 1-methylbenzalacetophenone, crotonaldehyde, cinnamaldehyde, methyl vinyl ketone and/or an α,β-unsaturated polyester diol prepared by polycondensation of maleic acid, fumaric acid, methacrylic acid and/or acrylic acid with oligomeric diols such as butanediol, diethylene glycol, propylene glycol or 1,3-propanediol and/or triols such as glycerol and having a molecular weight factor per double bond of from 150 to 3000, a functionality of from 2 to 6, a hydroxyl number of from 20 to 800 and an acid number of from 0 to 15.

4. A process as claimed in claim 1, wherein (i) is used in an amount of from 0.01 to 20% by weight, based on the weight of the polyurethane foam.

5. A polyurethane foam obtainable by a process as claimed in claim 1.

6. A polyurethane foam comprising products of the reaction of primary and/or secondary amines with α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid derivatives, α,β-unsaturated ketones and/or α,β-unsaturated aldehydes.

7. The use of α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid derivatives, α,β-unsaturated ketones and/or α,β-unsaturated aldehydes in polyurethane foams having a reduced primary amine content.

8. The use of α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid derivatives, α,β-unsaturated ketones and/or α,β-unsaturated aldehydes in polyurethane foams for reaction with primary amines.

Production of polyurethane foams

Abstract

In a process for producing polyurethane foams by reacting isocyanates with compounds which are reactive toward isocyanates in the presence of blowing agents and in the presence or absence of catalysts, additives and/or auxiliaries, the reaction is carried out in the presence of at least one of the following compounds (i): an α,β-unsaturated carboxylic acid, an α,β-unsaturated carboxylic acid derivative, an α,β-unsaturated ketone and/or an α,β-unsaturated aldehyde.

We claim:-

1. A process for producing upholstery for furniture or automobiles, mattresses, foam backing for carpets, polyurethane foams for backfoaming instrument panels or steering wheels or shoe soles based on flexible polyurethane foams by reacting isocyanates with compounds which are reactive toward isocyanates in the presence of blowing agents and in the presence or absence of catalysts, additives and/or auxiliaries, wherein the reaction is carried out in the presence of at least one of the following compounds (i): an α,β-unsaturated carboxylic acid, an α,β-unsaturated carboxylic acid derivative, an α,β-unsaturated ketone and/or an α,β-unsaturated aldehyde.

2. A process as claimed in claim 1, wherein the compound (i) used is $R^1R^2-C=CR^3COR^4$, where

R^1: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl,
R^2: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl,
R^3: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl,
R^4: H, C_1-C_{12}-alkyl, C_6-C_{20}-aryl, -O-C_1-C_{12}-alkyl, -O-C_1-C_{12}-alkyl-OH, -C_1-C_{12}-alkyl-OH, -O-C_1-C_{12}-alkyl, -O-C_1-C_{12}-alkyl-NH_2, -C_1-C_{12}-alkyl-NH_2,-O-Benzyl, -O-Aryl, -O-C_1-C_{12}-alkyl-COOH, -O-C_1-C_{12}-alkyl-CH(OH)-CH_2-O-(CO)-$CHCH_2$, -O-C_1-C_{12}-alkyl-O-(CO)-$CHCH_2$, -O-C_1-C_{12}-alkyl-CH(OH)-C_1-C_{12}-alkyl-O-C_1-C_{12}-alkyl-O-C_1-C_{12}-alkyl-CH(OH)-CH_2-O-(CO)-$CHCH_2$.

3. A process as claimed in claim 1, wherein the compound (i) used is acrylic acid, crotonic acid, isocrotonic acid, sorbic acid, fumaric acid, cinnamic acid, hydroxyethyl acrylate, 3-(acryloyl-oxy)-2-hydroxypropyl methacrylate, benzyl cinnamate, trans-3-nonen-2-one, benzalacetone, dibenzalacetone, benzalacetophenone, 1-methylbenzalacetophenone, crotonaldehyde, cinnamaldehyde, methyl vinyl ketone and/or an α,β-unsaturated polyester diol prepared by polycondensation of maleic acid, fumaric acid, methacrylic acid and/or acrylic acid with oligomeric diols such as butanediol, diethylene glycol, propylene glycol or 1,3-propanediol and/or triols such as glycerol and having a molecular weight factor per double bond of from 150 to 3000,

a functionality of from 2 to 6, a hydroxyl number of from 20 to 800 and an acid number of from 0 to 15.

4. A process as claimed in claim 1, wherein (i) is used in an amount of from 0.01 to 20% by weight, based on the weight of the polyurethane foam.

5. Upholstery for furniture or automobiles, mattresses, foam backing for carpets, polyurethane foams for backfoaming instrument panels or steering wheels or shoe soles based on flexible polyurethane foams obtainable by a process as claimed in claim 1.

6. Upholstery for furniture or automobiles, mattresses, foam backing for carpets, polyurethane foams for backfoaming instrument panels or steering wheels or shoe soles based on flexible polyurethane foams comprising products of the reaction of primary and/or secondary amines with α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid derivatives, α,β-unsaturated ketones and/or α,β-unsaturated aldehydes.

0050/049951

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

INVENTORSHIP IDENTIFICATION

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SPECIFICATION IDENTIFICATION

the specification of which

[ ] is attached hereto.

[ ] was filed on _____ as

Application Serial No. _____

and was amended on _____ (if applicable).

[x] was filed as PCT international application

Number PCT/EP00/03466

on April 17, 2000

and was amended under PCT Article 19

on _____ (if applicable)

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above–identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information known by me to be material to the patentability of this application in accordance with Title 37, Code of the Federal Regulations. §1.56(a).

[ ] In compliance with this duty there is attached an information disclosure statement. 37 CFR 1.97.

[x] In compliance with this duty, information which may be material is disclosed in the specification of the subject application.

CLAIM FOR BENEFIT OF EARLIER U. S. / PCT APPLICATION(S) UNDER 35 U. S. C. 120

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is / are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that / those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national of PCT international filing date of this application.

U. S. Application(s) (or PCT applications designating U. S.)

U. S. Application Serial No.	**Filing Date**	**Status (pending, patented, abandoned)**

RELATED FOREIGN APPLICATIONS

Related foreign applications, if any, filed in the name of the inventor(s) or the inventor(s) assigns more than twelve months before the filing of the subject application are as follows

Country	**Application No.**	**Date of filing**	**Date of issue or publication**

POWER OF ATTORNEY

I hereby appoint the following attorney(s) and agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith:

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CLAIM FOR BENEFIT OF FOREIGN PRIORITY UNDER 35 U. S. C. §119

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United State of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

[ ] No such applications have been filed.

[x] Such applications have been filed as follows

DETAILS OF FOREIGN APPLICATION FROM WHICH PRIORITY CLAIMED UNDER 35 U. S. C. §119

Country	Application No.	Date of filing	Date of issue or publication
Germany	*19919826.8*	*30 April 1999*	

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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